

A MILD, PROTECTIVE AND EFFICIENT PROCEDURE  
FOR GRINDING COAL: CRYOCRUSHING

by

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ABSTRACT

Conventional grinding methods are harsh and produce dramatic changes in coal. When coal, initially at room temperature, is ground in the presence of air, the high localized temperatures produced are known to cause both the production of gases and surface oxidation. These perturbations make meaningful measurements on the product very difficult. A technique that minimizes these effects is the pulverization of coal in liquid nitrogen. Compared with conventional methods, the process is rapid and appears to be less destructive chemically. ESCA measurements support this conclusion. Surface oxidation is significantly reduced by this mild treatment. The method produces more particles below 38 microns than does conventional grinding and these fine particles are less prone to agglomeration.

The crushing of coal presents a considerable challenge to the experimentalist interested in obtaining valid, representative measurements of coal properties. From the moment the coal is broken from the mine face, it begins changing its physical and chemical properties. Not the least of these alterations are the evolution of gases and surface oxidation. By the time the coal reaches the laboratory, it has undergone changes comparable to those it will experience en route to gasification/liqefaction plants. To this extent, the laboratory analyst is dealing with a material similar to that used in these industrial processes. However, further grinding of the coal for laboratory purposes can modify the coal significantly. Radd, Carel and Hamming<sup>2</sup> have shown that olefinic gases are evolved during the process, presumably as a result of the grinding process itself. This suggests that conventional grinding processes<sup>3,4</sup> are harsh and produce important changes in coal. The production of heat and the increase of reactive surfaces in an oxidizing environment further modify the coal and make its similarity to the material encountered by the engineers more remote. Thus, every effort must be made to minimize these

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<sup>1</sup>On sabbatical leave, Philadelphia College of Pharmacy and Science, Philadelphia, Pa.

<sup>2</sup>F. J. Radd, A. B. Carel and M. C. Hamming, submitted to Fuel.

<sup>3</sup>G. C. Lowrison, "Crushing and Grinding," Butterworth, p. 33, 1974.

<sup>4</sup>D. I. Hurth, L. S. Sundae and C. W. Schultz, U.S.B.M.R.I. 8069, Twin Cities, Minn., 1975.

effects. A technique discovered independently in this laboratory and recently reported elsewhere<sup>5,6</sup> appears to achieve this.

#### EXPERIMENTAL WORK

Air-dried coal (approximately 0.65 cm stock) is placed in a Dewar flask containing liquid nitrogen. All but a few milliliters of the liquid nitrogen are decanted and the deep-frozen coal is transferred rapidly to a hammermill.<sup>7</sup> The issuing product, considerably below room temperature, is collected in a plastic bag and is surrounded by nitrogen vapors rising from the coal. This is in contrast to grinding using a mini-ball mill (Wiggle-bug Model LP60) where the issuing coal is hot to the touch. The ground samples are quickly transferred to a sieve<sup>8</sup> for sizing and sealing for later experimentation.

#### RESULTS AND DISCUSSION

While grinding of polymeric materials at reduced temperatures has been noted in the English literature,<sup>3</sup> this laboratory is unaware of any such study on coal. Recent abstracts in Japanese<sup>5</sup> and Russian<sup>6</sup> publications suggest many parallels to this work. These papers have been received and are being translated.

That precooling the coal to liquid nitrogen temperature produced dramatic effects on the ground product is evident from Table I. Samples (100 g) of Illinois No. 6 coal were ground under a variety of conditions: namely, in air at ambient temperature, with dry ice, and in liquid nitrogen. The ground coal was rapidly sieved into fractions between 500 and 90 microns, between 90 and 38 microns, and a fraction below 28 microns. The latter fraction was further analyzed with a Coulter Counter<sup>9,10</sup> and the results were presented in Table I. Whereas regular grinding, i.e., at initial ambient temperature in air, resulted in a particle size distribution that averages near the 90 micron size, those grindings at reduced temperatures produced average particles closer to the 38 micron size. Nearly a third of the coal that was freeze-ground in liquid nitrogen passed the 38-micron sieve compared with 7.7 percent for the regularly ground coal. These percentages are remarkably reproducible. Furthermore, the Coulter Counter study of the particle distributions showed the most probable particle size in this fraction to be 28 microns for the regular grind and 18 microns for

<sup>5</sup>E. Nakanichi and K. Toyotate Funsai (Micromeritics) 18, 94 (1973) via Chem. Abstr. 81, 171948.

<sup>6</sup>T. Khrenkova, V. Lebedev, N. Goldenko and G. Glovina, Khim. Tverd. Topl. 1975, 11; via Chem. Abstr. 83, 13132.

<sup>7</sup>Micropulverizer 67J1431, Slick Company, Summit, N.J.

<sup>8</sup>Type 03.501 #720 Manufactured by Alfred Fritch for the Geos Corporation.

<sup>9</sup>T. Allen, "Particle Size Measurement," 2nd ed., John Wiley & Sons, N.Y., 1975.

<sup>10</sup>We are indebted to F. Radd, Continental Oil Company, Ponca City, OK for these analyses.

TABLE I  
Particle Size Distributions Reported in Grams and as % Recovery

Sample	Size in Microns							Most Probable size -38 Fraction (Coulter Counter)
	+500 g	+500 %	-500 g	+90 %	-90 g	+38 %	-38 g	
Air (ambient)	---	---	21.5	34.7	35.7	57.6	4.8	28 microns
N <sub>2</sub> (k) (air-dried coal)	0.2	0.3	19.4	25.5	32.3	42.4	24.2	18 microns
N <sub>2</sub> (k) (wet coal)	---	---	18.9	26.6	27.0	38.0	25.2	not measured
N <sub>2</sub> (k) (double ground)	---	---	6.3	13.9	22.0	48.3	17.2	not measured
CO <sub>2</sub> (s)	0.1	0.2	19.9	37.0	23.5	43.5	10.5	not measured

\*After one week, agglomeration reduced this fraction by 40%.

\*\*After one week, agglomeration reduced this fraction by 10%.

the liquid-nitrogen-ground coal. The fraction ground at dry ice temperature was not subjected to Coulter Counter analysis but might be expected to be intermediate since the sieve classification is intermediate.<sup>4</sup>

It should be noted that care must be exercised both in the grinding process and in handling of the ground product. Considerable loss of ultra-fine coal dust was evident during the grinding. For health reasons as well as for scientific study, it would be advantageous to recover these colloidal particles, which could be a most valuable fraction; possibly a shrouded mill could be used. The surface properties of the -38 micron fractions were considerably different than those of other fractions. A second sieving for a longer period (thirty minutes versus the original ten minutes) showed that forty percent of the regularly ground coal failed to pass the 38 micron screen, whereas all but ten percent of the liquid-nitrogen-ground coal did so. Of course, one recovers more of the -38 micron fraction with further increases in sieving time, but this is likely due to the abrasive nature of the sieving process itself. Thus, it appears that the coal ground with liquid nitrogen is not only more friable, but is less prone to agglomeration.

Even under the mild grinding conditions produced by liquid nitrogen, some interaction with oxygen will occur. Coal has trapped in its inner pores<sup>2,10</sup> significant quantities of gases, about eighteen percent of which is oxygen. These gases are not removed by pumping under vacuum, but probably are released during the grinding operation. Some of these gases can be displaced by treating the coal with methanol, shown by Fugassi<sup>11</sup> to swell the coal structure. Experiments performed in this laboratory show that methanol releases three to ten cc of gas, predominantly air, at STP per ten grams of Illinois coal. The enormously increased surface produced when a 0.65-cm coal fragment (surface area ~2.5 cm<sup>2</sup>) is reduced to 25 micron cubes on edge (surface area 600 cm<sup>2</sup>) can scavenge a significant fraction of the oxygen liberated by the grinding process.

Such a dramatic increase in surface area caused by efficient grinding might be expected to result in major differences in the ESR spectrum of the ground product. However, no differences in the spectra of coal ground in liquid nitrogen and of coal ground in air were observed in any of the sieved fractions. Aging of coal ground in air did produce an increase in ESR absorption; presumably this was due to oxygen uptake. A study of this phenomenon is planned in the near future.

The most informative and startling experiment that distinguished the products of the two grinding methods involved sedimentation rates in a polar solvent mixture (1:1 toluene-methanol). Samples (0.5 g) of -38 micron fractions from the regular grind and the liquid-nitrogen grind were suspended in fifty cc of the solvent mixture. Although the liquid-nitrogen-ground sample had a smaller particle size, it settled out about 100 times as fast as the regularly ground coal. Because this striking difference

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<sup>10</sup>J. A. Solomon and R. J. Enright, Proceedings 8th Biennial Conference of the International Briquetting Association, pp. 61-71, Denver, CO., 1963.

<sup>11</sup>J. P. Fugassi and M. Mitchell, Jr., "Coal Science," Adv. Chem. Ser. 55, 400 (1966).

persists for several weeks, it reflects permanent changes in these samples. Our interpretation is that the regularly ground coal experienced extensive oxidation during the grinding and developed a more polar surface which interacts more strongly with the methanolic solvent so that the settling rate is reduced. Regardless of whether this explanation is correct, the experiment indicates a drastic difference in the surface-solvent interaction for these differently ground coal samples. The toluene-methanol extracts of these samples are being analyzed by HPLC for further comparison. An alternative explanation that is not supported by ESCA analyses (vide infra) is that the product ground in liquid nitrogen is less homogeneous, and results in more of the dense ash in the -38 micron fraction. However, since this fraction was nearly a third of the sample and greatly exceeds the ash content of Illinois No. 6 coal, it could provide only a partial explanation for the rapid settling rate of the liquid-nitrogen-ground coal.

The -38 micron fractions of air-ground and liquid-nitrogen-ground coal were submitted for ESCA analysis using a Hewlett-Packard Model 5950A photoelectron spectrometer equipped with an aluminum anode. The samples were heavily coated on double sticky tape and were evacuated overnight to  $\sim 1 \times 10^{-9}$  torr prior to analysis. Charging effects were minimized by flooding the sample with electrons and biasing it slightly negative. The data are presented in Figures 1 and 2 where the 50K (counts per inch) survey scans show an oxygen carbon ratio of 0.48 for the air-ground coal and a 0.25 ratio for the liquid-nitrogen-ground coal (using standard sensitivity factors).<sup>12</sup> Because of the low pressures involved and sample handling procedures, the oxygen analysis is believed to represent chemically bound oxygen and not adsorbed oxygen.<sup>13</sup> Further, the 5K insert scans show that there is not a significant concentration of silicon, aluminum, or sulfur in the liquid-nitrogen-ground coal. If an enrichment in these elements occurred, it was in the air-ground fraction. Finally, it should be observed that nitrogen incorporation onto the coal surface during grinding was negligible. The 5K insert scans suggest  $1.2 \pm 0.1$  atom-percent of nitrogen in both samples. This is consistent with the macroscopic elemental analysis. These spectra, coupled with the observation that the ESCA analysis for oxygen in the liquid-nitrogen-ground sample ( $\sim 20\%$ ) compares favorably with that by neutron activation ( $19.55 \pm 0.16\%$ )<sup>14,15</sup> suggests that the liquid-nitrogen-ground coal surface more accurately represents the bulk or macroscopic structure of the coal.

#### ACKNOWLEDGMENTS

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<sup>12</sup>C. D. Wagner, Anal. Chem., 44, 1050 (1972).

<sup>13</sup>D.C. Frost, W. Leeder, and R. Tapping, Fuel 53, 206 (1974).

<sup>14</sup>We are grateful to Professor Volborth, Department of Chemistry, North Dakota State University, Fargo, N.D. 58102, for these analyses.

<sup>15</sup>G. Miller and A. Volborth, "Use of 14-Mev Neutron Generator in Analysis of Coal and Coal Derivatives," Small Accelerator Conference, Denton, Texas, Oct. 25-27, 1976.

ESCA SPECTRA OF ILLINOIS NO. 6 COAL  
(-38 MICRON FRACTION, AIR-GRIND)

SENSITIVITY FACTOR: 50K  
(5K FOR INSETS)

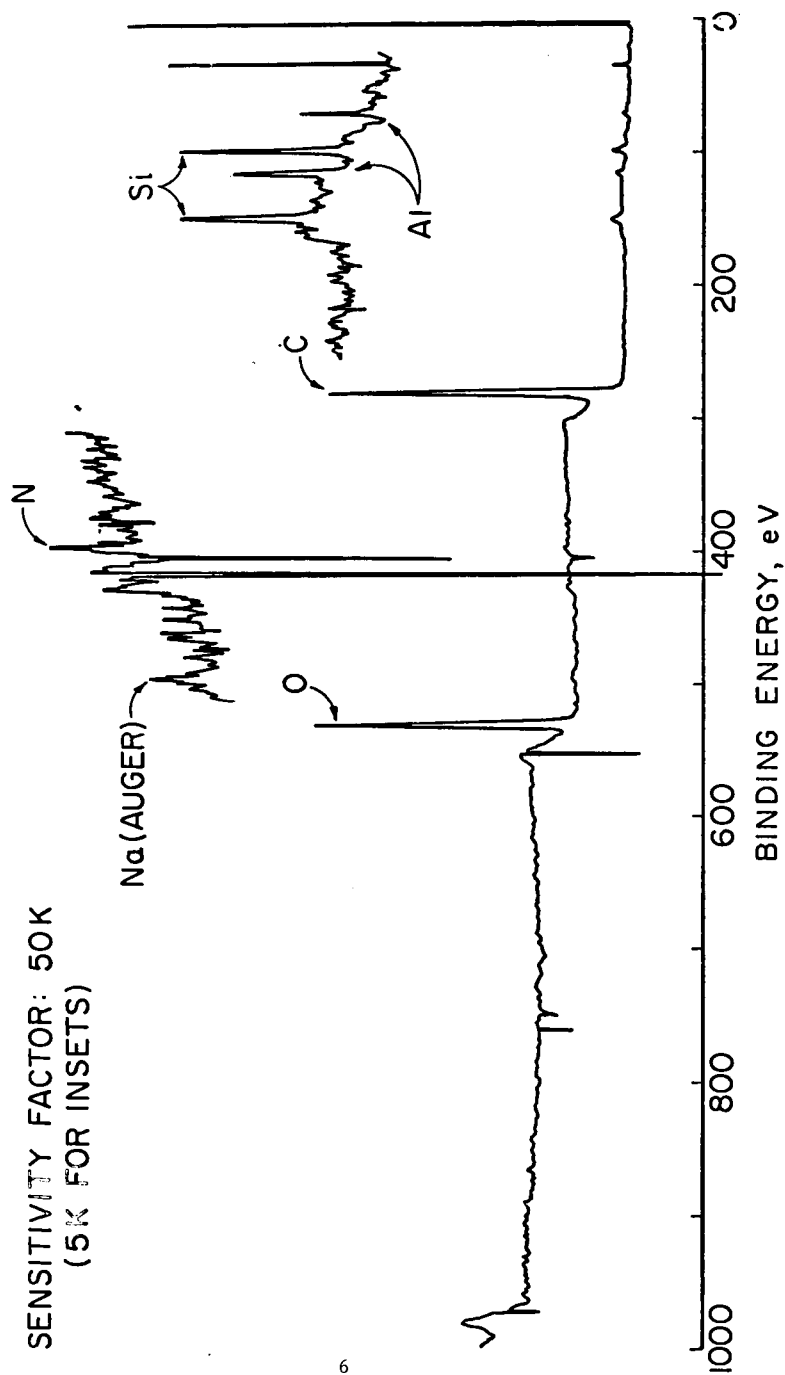


Figure 1

ESCA SPECTRA OF ILLINOIS NO. 6 COAL  
(-38 MICRON FRACTION, LIQUID N<sub>2</sub> GRIND)

SENSITIVITY FACTOR: 50 K  
(5 K FOR INSETS)

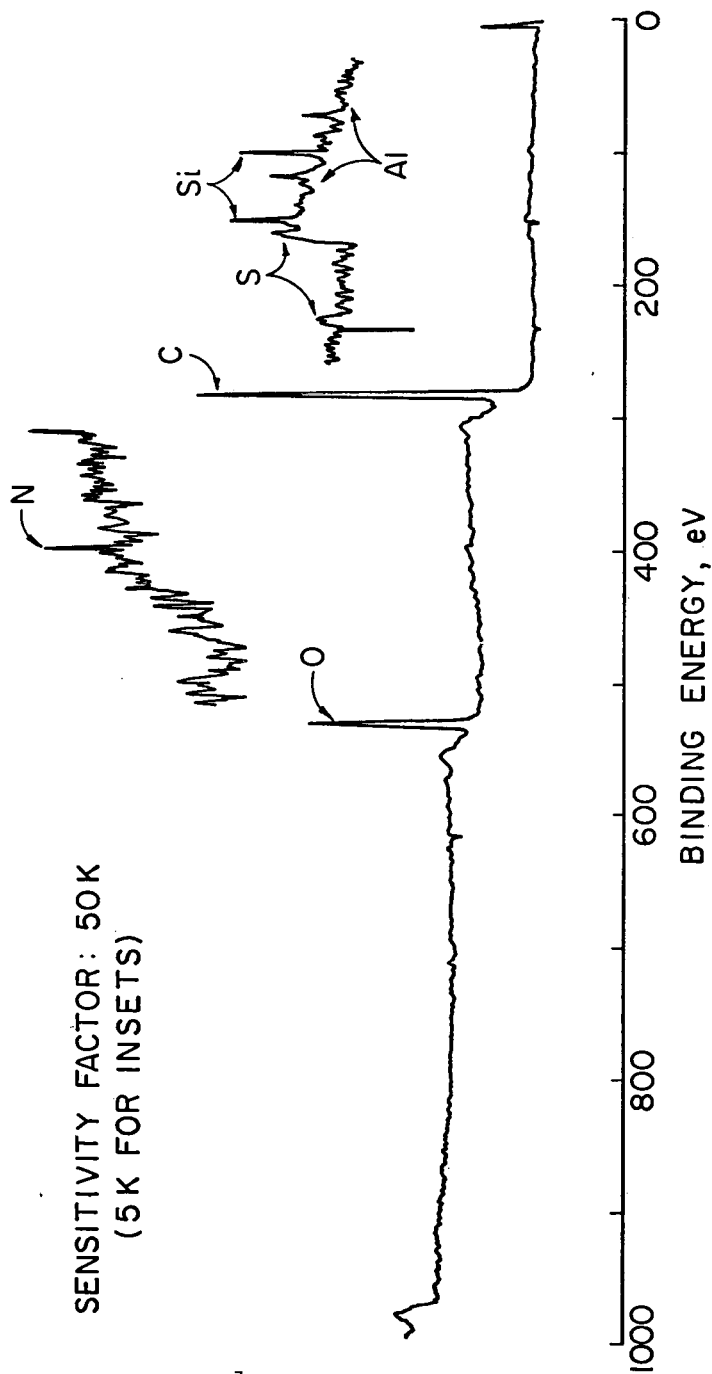


Figure 2